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(54) Title: INFILTRATED POWDERED METAL COMPOSITE ARTICLE

(57) Abstract

Precision molded articles, such as die cavities, pertaining to the field of powder metallurgy, and having high hardness and impact resistance, are made by combining granules of refractory and granules of a first metal or alloy which has a homogeneous crystalline appearance at a temperature below its melting point and a lower Rockwell Hardness than the refractory, mixing the granules with organic binder, molding the granule-binder mixture into a green molded preform, thermally degrading and removing the binder to form a skeletal preform, and infiltrating the preform with a second metal or alloy which will wet the first metal or alloy and has a lower Rockwell Hardness than the first metal or alloy, thereby forming a molded article having refractory granules fully enveloped within a single skeleton of the first metal or alloy, the refractory granules and skeleton being surrounded by layers or matrices of softer metals.

INFILTRATED POWDERED METAL COMPOSITE ARTICLE

Technical Field

This invention relates to powder metallurgy, metal composite materials containing impact resistant and abrasion resistant components, precision molded articles made from such materials, and a process for forming said articles.

Background Art

Powder metallurgy techniques have been used to formulate refractory metal composite materials with both high hardness and high impact strength. U.S. Patent No. 4,024,902 describes a composite material made from cemented carbide particles containing tungsten carbide and cobalt, the cemented carbide particles being placed in a mold and infiltrated with molten steel alloy. The tungsten carbide and cobalt dissolve in the steel alloy and then precipitate from the alloy as the article is cooled. The resultant composite article contains particles of tungsten carbide surrounded by successive shells containing tungsten (from the tungsten carbide), carbon (from the tungsten carbide), cobalt, and steel, each of these shells having lower hardness than the tungsten carbide particles. The remainder of the article is occupied by the steel alloy. The hardest material in such a composite is tungsten carbide, and the softest material in such a composite is steel alloy. U.S. Patent No. 4,140,170 describes an improvement in the molding process of U.S. Patent No. 4,024,902. According to the method of the latter patent, sintered tungsten carbide is ground up and mixed with iron powder. The powder mixture is then packed in a mold and heated to form a composite material. The methods of these patents employ liquid phase reactions which are not suitable for the precision replication of a molded shape, due to dimensional changes which occur as the materials within the composite

chemically combine with one another.

U.S. Patent No. 3,258,817 describes a composite
material made by placing spheroidal, refractory, hard
metal particles in a mold, infiltrating the particles with
5 a molten binder metal having a melting point between 816°C
and 1649°C, and cooling the infiltrated article. The
refractory particles partially dissolve in the binder
metal during infiltration, then precipitate from the
binder during cooling of the article. The process
10 conditions are said to be preferably controlled so as to
cause an "intergrowth" of the refractory granules and
formation of a continuous hard metal phase. Such a
composite material would have low impact resistance due to
the interconnection or intergrowth of refractory granules,
15 since this would provide an efficient pathway for crack
propagation through the material. Also, the method of
this patent might be unsuitable for the precision
replication of a molded shape due to the use of liquid
phase reactions.
20 U.S. Patent Nos. 3,823,002 and 3,929,476
describe precision shaped articles, such as electrical
discharge machining electrodes, made by molding in a
flexible mold a plastic mixture of multimodal refractory
powders and a thermoplastic binder to form a green molded
25 article of predetermined shape and dimensions, heating the
green molded article to remove the binder and consolidate
the refractory powders into an interconnected skeletal
structure, and infiltrating the resulting skeletal
structure with a molten infiltrant which is a low melting
30 point metal or alloy.

U.K. published Patent Application No. 2,005,728
A describes a molded, non-refractory metal article made by
molding in a flexible mold a plastic mixture of
non-refractory, spherical metal powders and heat-fugitive
35 binder comprising thermoplastic material to form a green
article of predetermined shape and dimensions, heating the
green article to remove the binder and consolidate the

non-refractory spherical powders in the form of a porous,
monolithic skeleton of necked particles of non-refractory
metal, infiltrating the skeleton with a molten metal
having a melting point that is at least 25°C less than the
5   melting point of the lowest melting of the spherical,
non-refractory particles, and cooling the metal
infiltrated skeleton thereby forming a homogeneous,
void-free non-refractory metal article of two intermeshed
metal matrices. The molded skeleton may be made of
10   particles of Fe, Co, Ni, or their alloys and the
infiltrant metal may be Cu, Ag, or Sn.

Disclosure of Invention

The present invention provides, in one aspect, a
metal composite article comprising first and second
15   intermeshed matrices, said first matrix comprising
granules of a refractory and said second matrix comprising
a continuous metallic phase, said article being substan-
tially free of voids, characterized in that:

(a) said refractory granules have a mean
20   diameter of 1 to 100 micrometers and said refractory
is

(i) metal carbide, boride, oxide,
silicide, or nitride, or
(ii) metal selected from the group
25   consisting of tungsten, molybdenum, tantalum,
niobium, vanadium and titanium, or
(iii) combinations thereof;
(b) said first matrix further comprises a
monolithic skeleton comprising a solid first metal or
30   alloy which has a homogeneous crystalline appearance
at a temperature below its melting point when viewed
under an optical microscope and has lower Rockwell
hardness than said refractory, said first metal or
alloy fully enveloping said refractory granules, the
35   latter being uniformly dispersed in said skeleton;
and

(c)   said continuous metallic phase of said
second matrix occupies the connected porosity in said
skeleton, said continuous phase further comprising a
solid second metal or alloy which wets said skeleton,
5   has a Rockwell hardness less than or equal to the
Rockwell hardness of said first metal or alloy, and
has a melting point below the melting point of said
first metal or alloy.

Brief Description of Drawing

10   In the accompanying drawing, FIG. 1 is a
schematic diagram of a portion of an article of this
invention;

FIG. 2 is a flow diagram showing the manufacture
of a precision shaped article of this invention;

15   FIG. 3 is a pen-and-ink sketch of an optical
micrograph of an article of this invention; and

FIG. 4 is a view in perspective of a molded die
cavity of this invention.

Detailed Description

20   In the practice of this invention, a replicating
master of the desired shape and size is used to prepare a
flexible rubber mold. Next, granules of said refractory
metal carbide, boride, oxide, silicide, nitride, or the
aforementioned refractory metals, or said combinations
25   thereof (viz., component (a) above, hereafter referred to
collectively as "refractory" or "refractory granules") are
mixed with granules of said first metal or alloy (viz.,
that of skeleton (b) above, hereafter referred to
collectively as the "first metal"). The resulting powder
30   mixture is mixed with a heat fugitive binder and the
powder-binder mixture is then placed in said mold and
thereby molded into a shape that is the same as the
desired final shape. The powder-binder mixture is cured
in the flexible mold and the resulting cured, molded
35   "green" article is demolded and heated to thermally

degrade and remove essentially all of the binder. The
resulting porous molded shape or "preform" is then
infiltrated at a temperature below the melting point of
the first metal with said second metal or alloy (hereafter
5   referred to as the "infiltrant"). During the infiltration
step, contiguous granules of the refractory and the first
metal undergo sintering by volume diffusion, whereby the
first metal granules lose their original particle shape
and merge or consolidate to form a monolithic skeletal
10 structure which fully envelopes or surrounds the
refractory granules. The first metal granules thereby
undergo extensive change in their original shape. The
elements of the skeleton are in turn surrounded by the
infiltrant. After cooling the final article, the
15 infiltrated skeleton corresponds in shape to that of the
replicating master. In this skeleton, the connected
porosity (i.e., void space which is not sealed off or
isolated from porosity which communicates with the
exterior of the skeleton, in·contrast to "closed porosity"
20 which is inacessible void space wholly within the body of
the skeleton) is occupied by the infiltrant. The
infiltrated, molded article contains dispersed (i.e., not
interconnected) refractory granules, each of which is
surrounded by a gradient microstructure of materials of
25 lower hardness and greater impact strength. The article
as a whole exhibits high abrasion resistance, high
hardness, and high impact strength, and is a faithful
replica of the master used to prepare the mold from which
the molded preform was made.
30   By "gradient microstructure" is meant a
heterogeneous crystalline structure containing a plurality
of contiguous crystalline regions, each in the form of a
shell or plurality of contiguous shells surrounding,
encircling, or enveloping a refractory granule, the shells
35 exhibiting a progressive, gradual change with respect to
physical properties, such as Rockwell hardness and impact
strength, as measured radially outward from any individual

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refractory granule. Such a gradient microstructure
results in a composite article having bulk physical
properties which in total are not exhibited by any single
component (viz., the refractory, first metal, or
5   infiltrant) within the composite article.

The volume diffusion phenomenon mentioned above
is a solid state reaction which occurs below the melting
point of the first metal. The manner in which this
reaction occurs may be described as "particle encirclement
10 by diffusional transport means" and is believed to be
previously unknown in the art of powder metallurgy.
Despite the extensive change in shape of the granules of
first metal which occurs, and the consolidation of the
granules of first metal into a monolithic skeleton, the
15 finished composite article of the present invention
exhibits surprisingly little change in shape or size, when
compared to the dimensional changes typically encountered
in iron-containing powdered metal composite articles.

The gradient microstructure of a molded article
20 of the present invention can be further understood by
reference to FIG 1. Referring to FIG 1, shown in
schematic view are refractory granules 11. These
refractory granules are fully enveloped by first metal 15.
First metal 15 is in turn surrounded by infiltrant 19 (the
25 second metal). The refractory granules are not in contact
with infiltrant 19.

Optionally, one or more layers or shells of an
intermediate composition of refractory together with first
metal, such as layer 13, are disposed between refractory
30 granules 11 and first metal 15. These intermediate layers
of refractory together with first metal may tend to form
under some process conditions between the refractory
granules and first metal if the refractory is soluble in
the first metal. The presence of intermediate layers of
35 refractory together with first metal is not required in
this invention. When present, intermediate layers of
refractory together with first metal tend to improve the

impact resistance and hardness of the final molded
composite articles of this invention by making more
gradual the change in impact resistance and hardness
between the first metal and refractory within the
5   microstructure of the final article.

Optionally, one or more layers or shells of
intermediate alloy, such as layer 17, are disposed between
the first metal and infiltrant. These·intermediate layers
may tend to form under some process conditions if the
10   principal metal of the infiltrant (or an alloying metal
present therein) is reactive with the first metal. The
presence of intermediate alloy layers such as layer 17 is
not required in this invention. When present, such
intermediate layers tend to improve the impact resistance
15   and hardness of the final molded composite articles of
this invention by making more gradual the change in impact
resistance and hardness between the infiltrant and· first
metal within the microstructure of the final article.

When a representative metallurgically-prepared
20   cross-section of the article of this invention is examined
with a light microscope at a magnification at which said
two matrices are discernible, e.g., 150X, the refractory
granules are essentially uniformly distributed throughout
the skeleton formed by the first metal, and the first
25   metal and infiltrant are essentially uniformly distributed
throughout the article. Of course, at much higher
magnifications, the refractory granules, first metal, and
infiltrant may no longer appear to be uniformly
distributed within the field of view. There is no unique
30   axis or densification of the refractory granules in any
portion of the skeleton (especially in the peripheral
portion, i.e., the portion adjacent the surface of the
article), such as that otherwise indicative of the use of
pressure to shape the final article. The molded articles
35   of the present invention are essentially free of interior
and surface defects, such as voids or pits, and exhibit
physical, chemical, electrical and·mechanical properties

which are uniform from article to article.

Minimal shrinkage occurs during sintering of the
skeleton and infiltration thereof, the amount of such
minimal shrinkage depending upon the process parameters

5   chosen. With compensation for process shrinkage, a
precision tolerance, i.e. the percent deviation of the
dimensions of the final infiltrated article from blue
print specification, of within less than about $\pm$ 0.2% can
be obtained, e.g. $\pm$ 0.1%.

10   The uniform properties from article to article
and precision tolerance of the articles of this invention
means that these articles are particularly well-suited for
applications where high hardness, wear and impact
resistance, and close dimensional tolerances are

15   desirable, such as articles with intricate or complex
shapes and surfaces with fine details, e.g. stamping and
injection molding die cavities which are used to make
metal or plastic parts whose shape corresponds to the
shape of the die. Articles prepared according to the

20   present invention can exhibit Rockwell hardness greater
than about 50 together with Charpy unnotched impact
strengths greater than about 15 joules (11 ft.lbs.).

The replicating master used to prepare molded
articles according to the present invention can be made in

25   a conventional manner from wood, plastic, metal, or other
machinable or formable material. If a molded article
prepared according to the process of the present invention
exhibits significant dimensional change (e.g. shrinkage)
then the dimensions of the replicating master can be

30   adjusted (e.g. made larger) to compensate for those
dimensional changes occurring during processing. Such
adjustment may be desirable in the manufacture of large
articles of this invention, such as articles with a volume
of 1 liter or more.

35   The molding materials which can be used to
prepare a flexible mold in the process of this invention
are those which cure to an elastic or flexible rubbery

form and generally have a Shore A durometer value of about
25-60, and reproduce the fine details of the replicating
master without significant dimensional change, e.g.
without more than 1 percent linear change from the
5   replicating master. The molding materials should not be
degraded when heated to molding temperatures, e.g. 180°C,
and desirably should have a low cure temperature, e.g.
room temperature. A low temperature curing molding
material will form a mold which exhibits a close
10   dimensional control from master to mold, while a high
temperature curing molding material will generally produce
a mold having dimensions which differ undesirably from
those of the master. To maintain dimensional control, it
is preferable that the mold material have a low
15   sensitivity to moisture. Examples of suitable molding
materials are curable silicone rubbers, such as those
described in Bulletin "RTV" 08-347 of January, 1969, of
the Dow Corning Co., and low exotherm urethane resins.
Such molding materials cure to an elastic or rubbery form
20   having a low post cure shrinkage. The molding material
can be optionally reinforced by the addition of about 30
volume percent of less than 44 micrometer diameter glass
beads which may improve dimensional control in the molding
process.
25   The amount of molding material used to form a
mold of the replicating master can vary depending on the
particular molding material used and the shape of the
replicating master. It has been found that about 10 to 14
cubic centimeters of molding material for each cubic
30   centimeter of the replicating master will form a mold
which retains the desired flexible properties and also has
sufficient strength to support the small hydrostatic head
produced by the warm powder-binder mixture in the mold
before solidification of the binder.
35   The molding conditions, hereinafter discussed,
for molding the articles of this invention permit the use
of an inexpensive, soft, elastic or rubbery mold because

the only pressure applied is the hydrostatic head of the
warm powder-binder mixture in the mold, which pressure is
very small and causes negligible distortion. The mild
molding conditions thus help ensure a precisely molded
5   green article even though a highly deformable mold is
used. In addition, the molding technique results in a
molded green article with a uniform density.

The refractory granules are preferably present
in the final molded, infiltrated article in amounts less
10   than about 15 volume percent. If the refractory granules
have a mean diameter of approximately 50 micrometers, then
the refractory granules are preferably present in amounts
between about 5 and about 15 volume percent. If the
refractory granules have a mean diameter of about 15
15   micrometers or less, then the refractory granules are
preferably present in amounts between about 2 and about 15
volume percent. Larger amounts of refractory can be
employed when higher abrasion resistance is desired in the
infiltrated article, but the impact strength of such an
20   article may be lower, because excessive loadings of
refractory granules lead to contiguous packing of
refractory granules and an article which is more prone to
crack propagation throughout its interior. For an optimum
relationship of impact resistance and hardness, less than
25   15 volume percent, and preferably about 8 to about 13
volume percent, of the final article is refractory. The
refractory granules used to make the final molded article
can be regularly or irregularly shaped particles having an
original mean diameter of about 1 to about 100
30   micrometers, preferably about 1 to about 50 micrometers,
most preferably about 1 to about 25 micrometers (as
determined by Coulter Counter). Use of refractory
granules having a low original mean diameter results in
formation of a final shaped article having a smooth
35   surface finish. However, if substantial quantities of
refractory granules having a mean diameter less than about
1 micrometer are used, formation of the desired gradient

microstructure apparently cannot be obtained.

Suitable refractory granules useful in this invention include elemental refractory metals such as W, Mo, Ta, Nb, V, and Ti, carbides of metals such as B, W, Mo, Si, Ti, V, Nb, Ta, and Cr, borides of refractory metals such as Ti, Zr, and V, oxides of metals such as Al, Zr, Hf and Si, silicides of refractory metals such as W and Mo, and nitrides of metals such as ·Al. The chosen refractory should have a sufficiently limited solubility in the first metal so that the refractory granules do not completely dissolve in the first metal during processing of the composite article. Also, the refractory should desirably be sufficiently stable to withstand the processing conditions and temperatures at which infiltration is carried out without undergoing decomposition. This processing consideration can be satisfied by examining equilibrium solubility and rate of solubilization data for a given refractory-first metal combination, or by empirically infiltrating, sectioning and examining one or more test composite articles and noting the change in refractory granule size which takes place during infiltration. Tungsten carbide is the preferred refractory in a composite article in which the first metal is iron or ferroalloy.

The first metal is solid and must be homogeneous at a temperature below its melting point. By "solid" is meant that the first metal in the final article is a solid at room temperature. By "homogeneous" is meant that at some temperature below the temperature at which the first metal liquifies, the first metal must form a crystalline solid solution which has a homogenous crystalline appearance when viewed under an optical microscope. The first·metal need not be homogeneous at room temperature and need not be homogeneous at all temperatures below its melting point. It merely must be homogeneous at some temperature below its melting point without phase separation. The first metal must also have a Rockwell

hardness less than the Rockwell hardness of the refractory as measured under similar test conditions using ASTM E-103-61 (Reapproved 1979). Also, the first metal must be capable of undergoing volume diffusion at some temperature

5   below its melting point when in admixture with the refractory granules and the liquefied infiltrant. By "volume diffusion" is meant a solid-state sintering reaction occurring during heating of contiguous metal particles. Volume diffusion (sometimes referred to as

10 "lattice diffusion") is characterized by the spontaneous movement of atoms or molecules from the interior of contiguous metal particles to the previously unoccupied space between contiguous metal particles. Volume diffusion can be recognized by the occurrence of "necking"

15 between contiguous metal (i.e., formation of an enlarged contact area with a concave edge profile) and by a concurrent change in the shape of the remaining (unnecked) outer surface of contiguous metal particles. Volume diffusion may be contrasted with a different solid-state

20 sintering reaction referred to as "surface diffusion". Surface diffusion is characterized by the spontaneous movement of atoms or molecules from the surface of contiguous metal particles to the previously unoccupied space between contiguous metal particles. Surface

25 diffusion can be recognized by the occurrence of necking without a concurrent change in the shape of the remaining (unnecked) outer surface of contiguous metal particles. The necking and particle shape change phenomena referred to above are generally detected by sectioning and

30 polishing a sintered, cooled powdered metal composite and examining the polished surface under optical magnification.

The processing conditions necessary to promote volume diffusion in an article of this invention may tend

35 to vary as the shape or volume of that article is altered. Volume diffusion is both time and temperature dependent, and is more likely to take place as the time and/or

temperature at which infiltration is carried out is
increased. If an infiltrated article undergoes only
surface diffusion, it will have less than optimum impact
resistance because the refractory granules will not become
fully enveloped by the first metal, and in the final
5   infiltrated article the refractory granules will be in
contact with the infiltrant. In the practice of this
invention such contact is essentially avoided in the final
infiltrated article in order to obtain optimum physical
properties. The volume diffusion described above occurs
10   in this invention at relatively low temperatures,
conducive to maintaining dimensional stability in the
infiltrated article.

        The first metal is present in the final shaped,
infiltrated article in amounts between about 35 and about
15   70 volume percent, preferably in amounts between about 57
and about 62 volume percent. The granules of first metal
used to make the final molded article can be regularly or
irregularly shaped particles having an original mean
diameter of about 1 to about 100 micrometers, preferably
20   about 1 to about 44 micrometers. Suitable first metals
include powdered iron, powdered ferro alloys and other
metals which satisfy the above homogenity, Rockwell
hardness, and volume diffusion criteria, such as "1018"
(see AISI type 1018) low carbon steel, molybdenum, nickel,
25   manganese, and cobalt. Copper can be used as the first
metal if a lower melting metal or alloy (such as some
copper alloys) is used as the infiltrant. A powdered
ferro alloy known as "A_6" tool steel (see AISI type A_6)
having a typical composition 94.7% Fe, 2.25% Mn, 1.35% Mo,
30   1.0% Cr, 0.7% C, and 0.3% Si is most preferred.

        Organic binders suitable for use in this
invention are those which melt or soften at low
temperatures, e.g. less than 180°C, preferably less than
120°C, thereby providing the metal powder-organic binder
35   mixture with good flow properties when warmed and yet
allowing the powder-binder mixture to be solid at room

temperature so that a green article molded therefrom can
be normally easily handled without collapse or
deformation. The binders used in this invention are those
which are heat fugitive, that is, which burn off or

5   volatilize when the green molded preform is heated.
Preferred heat fugitive binders degrade without causing
internal pressures on the resulting skeletal preform
(which promote internal fractures) and without leaving
substantial binder residue in the skeletal preform.

10   Preferably, during heating of the molded mixture of
refractory granules and powdered first metal, the chosen
binder gradually degrades or decomposes at a low
temperature and leaves a minimal carbonaceous residue.

                    Organic thermoplastics or mixtures of organic
15   thermoplastics and organic thermosets are used as binders.
Thermoplastic materials generally leave lower carbonaceous
residues than thermoset materials when thermally degraded.
However, use of a thermoset-containing binder yields a
molded powder-binder shape with a higher green strength

20   and may offer manufacturing advantages. The use of a
mixture of thermoplastic and thermoset binder is
advantageous when large composite articles are prepared,
such as articles in which some of the binder degradation
products must escape from the internal portion of the

25   article through a distance greater than about 2 cm. In
such cases, a step-wise burn-off of the binder is
preferred in order to avoid a spontaneous exotherm of the
binder which could generate internal pressure resulting in
multiple internal fractures in the molded article. Such a

30   step-wise burn-off is carried out by heating the green
molded article to two or more successive temperatures,
those temperatures being the individual decomposition
temperatures of the thermoplastic and thermoset portions
of the binders. Alternatively, the thermoplastic portion

35   of the binder may be substantially removed by solvent
leaching followed by thermal degradation of the thermoset
portion of the binder.

A further alternative binder system employs a
diluent with the binder. The diluent volatilizes prior to
any significant binder degradation and thus provides open
passage for the thermal degradation products during
5 burn-off, reducing or elimating internal fractures in the
molded article.

Examples of thermoplastic binders include
paraffin, e.g. "Gulf Wax" (household grade refined
paraffin), a combination of paraffin with a low molecular
10 weight polyethylene, mixtures containing oleic or stearic
acids or lower alkyl esters thereof, e.g. "Emerest" 2642
(polyethylene glycol distearate, average molecular weight
of 400) as well as other waxy and paraffinic substances
having the softening and flow characteristics of paraffin.

15   Representative thermosetting binders which can
be used in combination with thermoplastics include epoxide
resins, e.g. diglycidyl ethers of bisphenol A such as
2,2-bis[p-(2,3-epoxypropoxy)phenyl] propane, which can be
used with appropriate curing catalysts. Care must be
20 exercised so as not to thermally induce cross-linking
during the mixing and molding steps when thermosetting
binders are used.

Representative solvents which can be used for
leaching out the thermoplastic portion of a thermoplastic
25 and thermoset binder mixture are ketones such as acetone
or methyl ethyl ketone, and aqueous solvents. Diluents
for use with "diluted" binder systems include liquids
which are good solvents for the uncured binder but poor
solvents for the cured binder. The diluent should not be
30 absorbed by the flexible molding material. Also, the
diluent should have a sufficiently high boiling point so
that it does not boil away before curing or setting of the
binder, and a sufficiently low boiling point so that the
diluent volatilizes before the binder begins to thermally
35 degrade. Preferred diluents are those which volatilize at
temperatures of about 150°C to 210°C, such as low
molecular weight polyoxyglycols and light hydrocarbon

oils. A preferred diluent is 1,3-butanediol (B.P. 204°C).

The infiltrant (i.e., the second metal) in the
final shaped article has a melting temperature below the
melting temperature of the first metal. Also, the

5   infiltrant is a solid in the final article at room
temperature. The infiltrant must also "wet" the skeleton.
Such wetting can occur either because the infiltrant wets
the first metal or because the principal metal component
within the infiltrant (or an alloying ingredient within

10   the infiltrant) reacts to form an alloy with the first
metal, which alloy coats the first metal and is wet by the
infiltrant. Wetting of the skeleton by the infiltrant can
be determined empirically (by testing to see if
infiltration occurs) or by determining if the infiltrant

15   will wet the first metal according to the sessil drop
test. Wettable combinations of infiltrant and first metal
will have a sessile drop test wetting angle of 90° or less
under a hydrogen atmosphere. The sessile drop test is
described, for example, in "Wetting of Ceramic Oxides by

20   Molten Metals under Ultra High Vacuum", F. L. Harding and
D. R. Rossington, J. Am. Cer. Soc. 53, 2, 87-90 (1970) and
in "The Wetting of TaC by Liquid Cu and Liquid Ag", S. K.
Rhee, J. Am. Cer. Soc. 55, 3, 157-159 (1972). The
empirical test is the most reliable indication that the

25   infiltrant will wet the skeleton, because the wetting of
the skeleton which occurs may be due to the above
described formation of intermediate alloys of first metal
with infiltrant (or an alloying ingredient present in the
infiltrant). Formation of such wettable alloys may be

30   difficult to predict in advance. However, the sessile
drop test is generally reliable and serves as a useful
guide in predicting whether or not the infiltrant will wet
the skeleton.

Also, the infiltrant has a Rockwell hardness

35   less than or equal to the Rockwell hardness of the first
metal, measured under similar testing conditions according
to the above ASTM test. Satisfaction of the above

hardness condition and satisfaction of the first metal
hardness condition mentioned earlier requires that in an
article of this invention, the refractory has the highest
hardness in the composite article, the first metal has an
5 intermediate hardness, and the infiltrant has the lowest
hardness. Because hardness and impact strength are
inversely related, the infiltrant has an impact strength
which is higher than the impact strength of the first
metal, measured according to ASTM E-23-72 (Reapproved
10 1978).

Preferably, the first metal and infiltrant are
not substantially soluble in one another, although this is
not required for the practice of the present invention.

The infiltrant occupies about 15 to about 50
15 volume percent, and preferably 25 to about 35 volume
percent, of the final molded, infiltrated article. The
infiltrant can be used in any convenient form (e.g.,
granules, sheets, foil, or beads) as it is melted during
infiltration of the skeleton. Suitable infiltrants
20 include copper, copper alloys, copper-manganese alloys,
silver, silver alloys, tin, tin alloys, iron, and
multicomponent alloys such as ferroalloys. Copper and
copper alloys are preferred infiltrants, especially when
iron or ferroalloy powders are used as the first metal.
25 In addition, when such iron or ferroalloy powders are used
as the first metal, then copper-manganese alloys
containing about 4 to about 35 weight percent manganese
are a preferred infiltrant. The presence of manganese in
the infiltrant results in the formation of intermediate
30 layer of austenitic iron at the interface between the
first metal and infiltrant and the enhancement of the
gradient microstructure within the final molded article.
Other alloying ingredients can be added to the infiltrant
to enhance the properties of the final molded article.
35 For example, in an article of this invention containing
iron or ferroalloy first metal and copper alloy
infiltrant, the presence of boron, magnesium, or silver as

alloying ingredients will enhance the fluidity of the
molten infiltrant. The presence of nickel and tin as
alloying ingredients in such an article will enhance the
toughness of the article through promotion of spinodal
5   decomposition as the infiltrant cools. The presence of
iron as an alloying ingredient in such an article will
decrease the corrosive action of the infiltrant upon the
skeleton and thereby improve the dimensional stability of
the molded article. Silicon, when present as an alloying
10   ingredient in such a system, will act as a deoxidizer for
the other alloying ingredients of the infiltrant.

The articles of this invention can contain other
materials (e.g. dissolved gases) if such materials are
desired in order to alter the physical properties of the
15   final article. However, the presence of such materials is
not required in this invention, and the articles of the
invention can consist essentially of refractory, first
metal, and infiltrant.

When a skeletal preform containing the above
20   described refractory granules and powdered first metal is
placed adjacent the above described infiltrant and heated
above the melting point of the infiltrant, the infiltrant
will melt and "wick" into the interior of the preform.
Additional heating (to the temperature at which the first
25   metal undergoes volume diffusion) results in substantial
rearrangement of components within the composite by solid
state reactions involving refractory, first metal and
molten infiltrant. Granules of the first metal undergo
volume diffusion, merging with one another and enveloping
30   individual refractory granules. The first metal assumes
the form of a continuous skeleton within which are
enveloped the refractory granules. The infiltrant fills
the connected porosity of the skeleton, and is in contact
with the first metal but no longer in contact with the
35   refractory granules (which have become enveloped in the
first metal). On cooling, the rearranged composite
structure is preserved, thereby locking-in or retaining

the spaced position of the encircled refractory granules.
Optionally, at the interface between refractory granules
and the first metal, crystalline compositions of first
metal and refractory can form into one or more
5   intermediate concentric shells or zones surrounding an
individual refractory granule. In addition, if the
infiltrant contains a component which will react with the
first metal (e.g., when manganese is present in the
infiltrant and the first metal contains iron), then, at
10 the interface between the first metal and infiltrant,
additional crystalline compositions of first metal and the
reactive infiltrant component can optionally form into one
or more intermediate shells or zones adjacent the first
metal and bulk of the infiltrant.

15   Examination of a polished metallurgical section
of a finished composite article of this invention under
optical magnification shows that the refractory granules
retain their original particle shape and spacing. The
particles of first metal lose their original particle
20 shape and become a continuous skeletal structure. The
finished composite article exhibits relatively little
dimensional change when compared to the master from which
the preform was molded. Dimensional change of a shaped
article of this invention prepared from tungsten carbide,
25 A_6 tool steel, and copper according to the present
invention is generally less than about 1 percent in any
lineal dimension, and preferably less than about 0.5
percent. This low degree of dimensional change is
surprising in view of the extensive dimensional change,
30 occuring as shrinkage of up to about 7 percent, which
occurs when a composite is prepared from granulated iron
infiltrated with copper.

            Shrinkage in the articles of this invention is
minimized in spite of the large amount of volume diffusion
35 occuring during infiltration. Volume diffusion is one
mechanism by which sintering is carried out in the art of
powder metallurgy. Other known sintering mechanisms

include viscous or plastic flow, evaporation and
condensation, and surface diffusion. All of these
sintering mechanisms generally promote shrinkage in the
sintered article. Sintering in the articles of this

5   invention appears to occur by a uniquely different
mechanism than that which is generally known to occur in
powder compacts or "green" parts. The formation of a
gradient microstructure occurs as a particle encirclement
by diffusional transport which takes place during

10   infiltration under solid state conditions, i.e., well
below the melting point of the first metal. The presence
of refractory particles which are greater than one
micrometer in size and the selection of first metal is
critical to maintaining dimensional stability in the final

15   article. As encirclement of refractory granules by the
first metal proceeds, a slight amount of shrinkage results
due to formation of the gradient microstructure. However,
shrinkage does not become excessive because a band of
first metal forms a continuous path between refractory

20   particles. The skeletal structure formed by the first
metal is insensitive to the erosive and corrosive action
of the infiltrant, and the spacing between individual
refractory granules remains constant, because part of the
narrow band or link of first metal between refractory

25   granules is not in contact with the infiltrant and does
not undergo further diffusion.

       The finished composite article has excellent
fidelity of replication when compared to the master from
which the preform was molded. Compositions prepared

30   according to the present invention have particular utility
in the manufacture of molded die cavities. Such molded
die cavities may be used in injection molding of plastics
or stamping of ductile metals which are formed into parts
having complex shapes corresponding to the shape of the

35   molded die cavity.

       The method of forming a composite article
according to the present invention involves mixing

refractory granules and powdered first metal with a heat
fugitive, organic binder, molding the powder-binder
mixture, setting or curing the mold contents, removing
the bulk of the binder, thereby forming a skeletal

5   preform, and infiltrating the preform with molten
infiltrant.

       Referring to FIG. 2, which illustrates a method
for forming an article of this invention, a replicating
master 101 is used to mold 102 a flexible form in the

10   desired shape by surrounding the master with an elastic,
rubbery, molding compound, and demolding 103 the master
from the cured solid rubbery mold 104. An admixture of
refractory granules 105 and powdered first metal 106 is
blended 107 to form a powder mixture 108 which is next

15   combined with a heat fugitive thermoplastic or
thermoplastic and thermosetting binder 109 and any
optional diluents 110 by mixing 111 (without causing
premature cure of the binder if a thermosetting binder is
used) in a blending device, e.g. a sigma blade mixer,

20   resulting in formation of a powder-binder mixture 112.
The refractory granules and powdered first metal are
uniformly dispersed in the binder matrix conducive to
forming a preform with homogeneous (i.e. uniform) density
which will be essentially uniformly porous when the binder

25   is thermally degraded.

       The flexible mold 104 is heated 114 and the
powder-binder mixture 112 fed directly to the heated mold
115. Optionally, instead of immediately molding the
powder-binder mixture, a mixture made with a thermoplastic

30   binder can be cooled 116 to a solidified mass 117 and
milled 118, preferably in a vacuum, to a granular or
free-flowing consistency ("pill dust" 119) for easy
handling and storage, and subsequently heated 120 to a
heated mass 121 at the time of the molding step. The

35   heated mold and its contents (the powder-binder mixture
111 or heated mass 121) are vibrated under vacuum 125 in
order to degas the mixture. The mold contents are allowed

to set or cure 126 and harden. The molded granule-binder
shape is demolded 127 by applying a vacuum to the outer
walls of the flexible mold. After demolding, the
resultant "green" molded preform 128 is a faithful replica
5   of the dimensions of the master. This molded shape has
good green strength and uniform density due to the
hardened matrix of binder which holds the refractory
granules and powdered first metal together.

If a mixture of thermoplastic and thermoset
10 binders was used to make the green molded preform, then
the thermoplastic binder can be partially removed from the
green molded preform by optionally leaching 129 the
preform in a solvent such as methylethylketone or water
for a period of about 4 to about 12 hours or less.
15
The green molded preform 128 is packed in a non-
reactive refractory powder, e.g. alumina or silica, to
prevent sagging or loss of dimension, and subsequently
heated 130 in a furnace to a temperature of about 780°C to
thermally degrade the binder. If mixtures of
20 thermoplastic and thermoset binders are used, or if
diluted binders are used, the heating step is carried out
in a series of stages in order to first remove those
materials which boil off or degrade at low temperatures,
followed by removal of the remainder of the binder.
25 During the heating step, the bulk of the binder is removed
from the article by vaporization and as gaseous products
of degradation, leaving a minute amount of amorphous
carbonaceous residue which may help to tack the refractory
granules and powdered first metal together. The
30 refractory granules, powdered first metal, and
carbonaceous residue form a rigid, handleable, skeletal
preform 131. The refractory granules and particles of
powdered first metal are in contiguous relationship. They
are interconnected or adhered together and essentially
35 retain their original particle shapes and relative
positions when viewed under optical magnification.

A skeletal preform made by the above heat
fugitive binder method will have minimal closed porosity.
The major portion of the void space in such a preform will
represent connected porosity. Only connected porosity can
5   be filled by molten infiltrant.

The preform is next infiltrated with the
infiltrant. The surfaces of the skeletal preform which
will be coincident with the working surfaces of the final
infiltrated article are preferably coated 132 with a
10   dispersion of zirconia in acetone in order to eliminate
overwetting, i.e. "beading" of infiltrant at those
surfaces of the skeletal preform. The infiltration step
135 is preferably carried out by supporting the skeletal
preform 131 and infiltrant (second metal) 136 in or on a
15   bed of alumina in a crucible, for example, one made of
graphite, alumina, or mullite. The infiltrant (in
solidified form) is placed in contact with the base of the
skeletal preform and heated above the melting point of the
infiltrant to a temperature at or above the temperature at
20   which the first metal undergoes volume diffusion, but to a
temperature below the melting point of the first metal.
Infiltration (and the attendant volume diffusion of the
first metal and encirclement of the refractory granules by
the first metal) is preferably carried out at the lowest
25   temperature at which volume diffusion is observed to
occur. The amount of infiltrant is usually chosen to be
slightly in excess of the amount necessary to fill the
connected porosity of the skeletal preform (as determined
by calculation or empirically). When the melting point of
30   the infiltrant has been reached, the infiltrant will melt
and "wick" into the interior (the connected porosity) of
the skeletal preform by capillary action. Heating is
continued until the temperature at which the first metal
undergoes volume diffusion is reached (this temperature
35   may be the same as the melting point of the infiltrant or
a higher temperature). The infiltrated preform is then
cooled 137, the infiltrated article 138 extracted, and any

excess zirconia coating is removed, e.g., by peening 139
with a glass bead peening apparatus (Empire Abrasive
Equipment Corp. Model No. S-20) at a pressure of 1.4 to
2.8 kg/cm^2 using an 8 mm diameter orifice. If an age

5   hardenable infiltrant is employed, e.g. copper alloyed
with nickel (15%) and tin (7%), or if the metal skeleton
is hardenable, the infiltrated article may be subjected to
a temperature aging cycle, using techniques well known in
the art of metalworking, to change the grain structure of

10   the interior or surface of the composite and increase the
hardness and/or wear resistance of the infiltrated
article. Finally, excess flashing is dressed off 140 and
any superfluous base material is machined or cut away from
the shaped working surface to produce the finished

15   infiltrated molded article.

        The time and temperature necessary to infiltrate
the preform and ensure that volume diffusion of the first
metal occurs will vary depending upon the choice of first
metal, the rate of heating, the gross dimensions of the

20   preform being infiltrated, the wetting characteristics of
the infiltrant, and the diameter of the pore-like passages
within the skeleton. These times and temperatures are
determined empirically using microscopic analysis of the
infiltrated sample. An infiltrated article which has been

25   insufficiently heated will not undergo volume diffusion.
Microscopic analysis of such an article will reveal that
the particles of powdered first metal have not lost their
original shapes and have not enveloped the refractory. An
infiltrated article which has been excessively heated may

30   undergo liquid phase reactions of the first metal due to
melting of the first metal. Microscopic analysis of such
an excessively heated article will reveal that the
refractory granules have been greatly reduced in size due
to reaction with the first metal. In addition, an

35   excessively heated article may be characterized by severe
distortion or dimensional change relative to the desired
master shape.

The resulting infiltrated molded article, such
as a copper infiltrated article, is substantially
void-free (i.e., it has a density at least 97% and usually
99% or more of the theoretical density based upon the
5 densities of the constituents of the preform and of the
infiltrant phase). Essentially the only uninfiltrated
space in such an infiltrated article is the closed
porosity of the original preform. The connected porosity
of the original preform is essentially completely occupied
10 by the infiltrant.

  The metallurgical structure of an infiltrated
molded article of the present invention can be further
understood by reference to FIG. 3. FIG. 3 is a
pen-and-ink drawing of an optical micrograph (taken at a
15 magnification of 750X) of a polished sample of the present
invention, prepared as described in Example 1. Tungsten
carbide granules 31 are surrounded by a thin shell or film
33 containing an alloy of iron, tungsten, and carbon.
Film 33 is further surrounded by an interconnected
20 skeletal iron matrix 35. Iron matrix 35 is in turn
intermeshed with copper matrix 37. When the article
depicted in FIG. 3 abrades against another surface,
tungsten carbide granules 31 provide good abrasion
resistance and high hardness. Tungsten carbide granules
25 31 will tend to protrude above the working surface of the
article depicted in FIG. 3 as that surface wears away.
Additional wear at the surface will result in the exposure
of new tungsten carbide granules 31. When the article
depicted in FIG. 3 receives an impact, the shock of that
30 impact will be transmitted into the interior of the
article. These shocks travel as shock waves which pass
through the tungsten carbide granules 31 and the metallic
materials 33, 35 and 37 of the article. Shock waves
passing from tungsten carbide granules 31 to alloy 33 are
35 dispersed due to the lower elastic constant (a factor
related to hardness) of the alloy 33. In turn, as those
shock waves pass through iron 35, and then copper 37, they

are further dispersed due to the lower elastic constant of
iron and copper. The hardest substance in such a
composite material is tungsten carbide, and the softest
(and most impact resistant) substance in such a composite

5 material is copper. There is an essentially smooth,
graduated change in hardness, impact resistance, and
energy absorbing ability throughout the material from the
tungsten carbide granules to the copper matrix. Due to
its microstructure and the gradient in hardness and impact

10 resistance from point to point within the composite, the
final molded article exhibits a high resistance to impact
(between that of the refractory and infiltrant) while
maintaining a high hardness (between that of the
refractory and infiltrant). The composite material shown

15 in FIG. 3 has particular utility as a molded die cavity.
        A molded die cavity prepared according to the
present invention can be further understood by reference
to FIG. 4. FIG. 4 is a perspective view of a molded die
cavity 41 having a base 43 and a working surface 44.

20 Female recess 45 lies in the end of cavity 41 opposite the
base and has indented surface 47 and scallops 49. The
shape of recess 45 corresponds to a male shape in the form
of a fluted wheel.
        Objects and advantages of this invention are

25 illustrated in the following examples but the amounts and
materials described in the examples, and various additions
and details recited therein, should not be construed to
limit the scope of this invention.

Example 1

30   A Charpy unnotched impact bar was machined to
the dimensions specified in ASTM E-23-72 (Reapproved
1978). A mold corresponding to this shape was made by
surrounding the bar with "RTV-J" curable silicone rubber.
The mold was cured and the bar removed from the mold.

35 Ninety grams of tungsten carbide granules having 1 to 15
micrometers mean diameter ("Type 111", commercially

available from Wah Chang Div. of Teledyne) and 210 grams
of powdered A₆ tool steel having a mean diameter less than
44 micrometers (commercially available from Stellite Div.
of Cabot Corp.) were dry mixed in a V-blender and heated
5   to 66°C. Thirteen grams of a polymer binder ("Emerest
2642", commercially available from Emery Industries) were
separately preheated to 66°C. The powders and polymer
binder were combined in a sigma blade mixer which had been
heated to 66°C. The mixture was milled for about 15
10   minutes and resulted in a thixotropic warm powder-binder
mixture containing approximately 27.7 volume percent
binder.

The warm powder-binder mixture and the flexible
rubber mold were heated to 66°C by storing them in a 66°C
15   oven for about 15 minutes. The warm powder-binder mixture
was then flowed into the warm flexible mold by vibratory
means. The mixture was deaired for 15 minutes with
continued vibration in a laboratory vacuum chamber
operated at 1 torr. The mold and contents were then
20   cooled to 0°C in a freezer and the hardened, "green"
molded preform subsequently extracted from the rubber mold
cavity using vacuum.

The green molded preform was placed in a
supporting bed of powdered alumina and heated in a
25   resistance heated box furnace with a dynamic argon
atmosphere. A temperature of approximately 400°C was
sufficient to volatilize and thermally degrade most of the
binder. Heating was discontinued when the temperature
reached 780°C, at which point the binder had completely
30   degraded and the skeletal particles in the matrix had
become tacked together.

The molded skeletal preform was removed from the
furnace after it had cooled to room temperature. An
acetone dispersion of zirconia (50% by volume) was applied
35   to all but one surface (the base) of the preform in order
to prevent the infiltrant metal from overwetting the
working surfaces. The base of the preform was then placed

adjacent 50 g of solid copper on a bed of alumina in an
open graphite crucible in a molybdenum wound electrical
resistance furnace. The furnace was evacuated to 0.1
torr, backfilled with nitrogen, purged and then refilled
5   with hydrogen to atmospheric pressure and maintained at a
flow rate of 0.5 liters/sec. The furnace was heated to
1083°C and held just above that temperature for 45 minutes
in order to carry out infiltration of the skeletal preform
by copper infiltrant and volume diffusion by the first
10   metal. The furnace was then turned off and allowed to
cool normally. Microscopic analysis of a metallurgically
prepared sample of this composite shows that the A_6 tool
steel surrounds the WC. Also, a definite and distinct
intermediate alloy of WC together with Fe can be seen
15   between the refractory and A_6.

Shrinkage was measured by comparing the master
shape to the final molded article. The article was tested
for abrasion resistance by sliding it across 220 grit
silicon carbide coated abrasive paper. Using hand
20   pressure, the article slid across the abrasive surface
much more freely than a similarly sized block of tool
steel having Rockwell hardness of 50. No scoring was
observed on the article of this invention, but scoring was
visually apparent on the tool steel block. The article
25   was tested for Rockwell C hardness and Charpy unnotched
impact according to ASTM E-103-61 (Reapproved 1979) and
ASTM E-23-72 (Reapproved 1978). The final molded article
exhibited the following characteristics:

Dimensional Change   -0.4%
30   Rockwell hardness (R_C) 49
Charpy unnotched impact (CIU) 15.1 joules (11.1 ft.lbs)

Examples 2 through 3

Using the method of Example 1, molded composite
articles were prepared by substituting various materials
35   for the A_6 powder used in Example 1. Set out below in
Table 2 are the first metal used, and the shrinkage,

Rockwell hardness, and Charpy unnotched impact values for
the resulting composite.

Table 2

Example	First metal	Dimensional change,%	R_C	CIU, joules
2	Fe	-0.35%	4 to 8	78.0 (57.5 ft.lbs.)
3	1018 steel	-0.095%	25 to 31	31.3 (23.1 ft.lbs.)

Examples 4 through 6

Using the method of Example 1, molded composite
articles were prepared using tungsten carbide refractory,
A_6 tool steel first metal, and two copper-manganese alloy
second metal infiltrants. Set out below in Table 3 are
the composition, shrinkage, Rockwell hardness, and Charpy
unnotched impact values for the resulting composite
articles.

Microscopic analysis of metallurgically prepared
samples of these composites shows that the A_6 tool steel
encircles the tungsten carbide. Also, a definite and
distinct intermediate alloy of manganese-steel alloy can
be seen between the A_6 tool steel and the copper-manganese
infiltrant. This intermediate alloy is austenitic iron, a
material known to have extreme toughness.

Table 3

Example	WC[a] %	A_6[a] %	CuMn alloy	Dimensional change,%	R_C	CIU, joules
4	40	60	Cu35Mn[b]	-0.41	33-44	56.4 (41.5 ft.lbs)
5	30	70	Cu35Mn[b]	-0.28	17-37	80.2 (59 ft.lbs)
6	30	70	Cu10Mn[c]	-0.30	20-44	26.4 (19.4 ft.lbs)

a. Weight percent based on the uninfiltrated skeletal preform. Final
   infiltrated articles contained about 32 to 34 volume percent infiltrant.
b. Cu35Mn is 65 weight percent Cu and 35 weight percent Mn
c. Cu10Mn is 90 weight percent Cu and 10 weight percent Mn

Examples 7 through 15

Using the method of Example 1, molded composite
articles were prepared by substituting several materials
for the refractory and first metal used in Example 1. The
5   composite articles were sectioned and analyzed to
determine whether or not the refractory particles had
become fully enveloped by the first metal. Set out below
in Table 4 are the refractory, first metal, infiltration
time and temperature, and whether or not the refractory
10 granules were fully enveloped by the first metal. Note
that in Examples 10 and 12 full envelopment did not occur,
but that an increase in infiltration temperature or
infiltration time brought about full envelopment of
refractory.

15

· Table 4

Example	Refractory	First metal	Infiltration time	temperature	Refractory fully enveloped?
7	TiB$_2$[a]	A$_6$[b]	12 hrs	1100°C	yes
8	WC+SiC[c]	A$_6$[d]	12 hrs	1100°C	yes
9	WC[a]	Mo+Fe[e]	12 hrs	1100°C ·	yes
10	WC[f]	M$_2$[g]	45 min	1100°C	no
11	WC[f]	M$_2$[g]	45 min	1250°C	yes
12	WC[f]	A$_6$[h]	15 min	1100°C	no
13	WC[f]	A$_6$[h]	45 min	1100°C	yes
14	B$_4$C$_3$[i]	Fe[j]	12 hrs	1100°C	yes
15	W[k]	Fe[l]	45 min	1100°C	yes

a   9 volume percent (v/o)

b   62 v/o

c   10 v/o WC + 2 v/o SiC

d   59 v/o

e   29 v/o Mo + 33 v/o Fe

f   13 v/o

g   58 v/o AISI type M$_2$, containing 0.82 v/o C, 0.3 v/o Mn. 0.2 v/o Si, 4.25 v/o Cr, 5 v/o Mo, 6.25 v/o W, 1.80 v/o V, balance Fe

h   58 v/o

i   10 v/o

j   61 v/o

k   11 v/o

l   60 v/o

Example 16

Using the method of Example 1, a molded composite article was prepared having 13 volume percent tungsten carbide refractory, 58 volume percent A$_6$ tool steel first metal, and 29 volume percent of a copper alloy infiltrant. The infiltrant contained 45 volume percent copper, 25 volume percent silver, 10 volume percent nickel, 5 volume percent iron, 12 volume percent tin, 1

volume percent boron, 0.05 volume percent magnesium, and
0.1 to 0.2 volume percent silicon. The resulting
composite article exhibited dimensional change of -0.32
percent, Rc of 52, and a charpy unnotched impact strength

5 of 15 joules (11 ft. lbs).

Various modifications and alterations of this
invention will be apparent to those skilled in the art
without departing from the scope and spirit of this
invention and the latter should not be restricted to that

10 set forth herein for illustrative purposes.

CLAIMS:

1.   A metal composite article comprising first
and second intermeshed matrices, said first matrix
comprising granules of a refractory and said second matrix
5   comprising a continuous metallic phase, said article being
substantially free of voids, characterized in that:
(a) said refractory granules have a mean
diameter of 1 to 100 micrometers and said refractory
is
10   (i)   metal carbide, boride, oxide,
silicide, nitride,
(ii) metal selected from the group
consisting of tungsten, molybdenum, tantalum,
niobium, vanadium, and titanium, or
15   (iii) combinations thereof;
(b)   said first matrix further comprises a
monolithic skeleton comprising a solid first metal or
alloy which has a homogeneous crystalline appearance
at a temperature below its melting point when viewed
20   under an optical microscope and has lower Rockwell
hardness than said refractory, said first metal or
alloy fully enveloping said refractory granules, the
latter being uniformly dispersed in said skeleton;
and
25   (c)   said continuous metallic phase of said
second matrix occupies the connected porosity in said
skeleton, said continuous phase further comprising a
solid second metal or alloy which wets said skeleton,
has a Rockwell hardness less than or equal to the
30   Rockwell hardness of said first metal or alloy, and
has a melting point below the melting point of said
first metal or alloy.

2.   An article according to Claim 1, further
characterized in that said refractory comprises metal car-
35   bide, said first metal or alloy comprises iron or
ferroalloy, and said second metal or alloy comprises
copper or copper alloy.

BUREAU

3.. An article according to any preceeding
claim, further characterized in that said refractory is
tungsten carbide.

4. An article according to any preceeding
5 claim, further characterized in that said refractory is 2
to 15 percent of the volume of said article, said first
metal or alloy is 35 to 70 percent of the volume of said
article, and said second metal or alloy is 15 to 50
percent of the volume of said article.

10   5. An article according to any preceeding
claim, further characterized in that said refractory is 8
to 13 percent of the volume of said article, said first
metal or alloy is 57 to 62 percent of the volume of said
article, and said second metal or alloy is 25 to 30
15 percent of the volume of said article.

6. An article according to any preceeding claim
further characterized in that said first metal or alloy
comprises iron or ferroalloy, said second metal or alloy
comprises copper and manganese, and said manganese is 4 to
20 35 percent of the weight of said second metal or alloy.

7. An article according to any preceeding
claim, further characterized in that said article has a
Rockwell hardness greater than 50 and a Charpy unnotched
impact strength greater than 15 joules.

25   8. An article according to any preceeding
claim, further characterized in that said article has a
density of at least 97 percent of the theoretical density
based upon the densities of said refractory, said first
metal or alloy, and said second metal or alloy.

30   9. An article according to any preceeding
claim, further characterized in that said refractory

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granules have a mean diameter of 1 to 15 micrometers and
said article is a die cavity.

     10. A process for forming a metal composite
article according to any preceeding claim, characterized
in that:

     (a) granules of a refractory having 1 to 100
micrometers mean diameter are blended with granules
of a first metal or alloy having 1 to 100 micrometers
mean diameter, said refractory being metal carbide,
boride, oxide, silicide, nitride or a metal selected
from the group consisting of tungsten, molybdenum,
tantalum, niobium, vanadium, and titanium, and said
first metal or alloy having a homogeneous crystalline
appearance at a temperature below its melting point
when viewed under an optical microscope and lower
Rockwell hardness than said refractory, thereby
forming a uniform mixture;

     (b) said uniform mixture is mixed with up to 50
volume percent of a heat fugitive, organic binder;

     (c) the resulting mixture is molded in a heated
flexible mold, said mold and its contents are cooled
to room temperature, and said contents are demolded
by applying a vacuum to the outside of said mold
thereby forming an essentially void-free green molded
preform having the size and shape of said mold;

     (d) said green molded preform is heated to
thermally remove said binder and form a rigid,
handleable skeletal preform;

     (e) said skeletal preform is placed in contact
with a second metal or alloy which will wet said
skeleton and which has a Rockwell hardness less than
or equal to the Rockwell hardness of said first metal
or alloy;

     (f) said skeletal preform is infiltrated with
said second metal or alloy by heating said skeletal
preform and said second metal or alloy above the

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melting point of said second metal, but below the
melting point of said first metal or alloy, whereby
said second metal melts and wicks into the connected
porosity of said preform by capillary action and said

5   first metal fully envelopes said refractory granules,
with the proviso that said refractory granules do not
completely dissolve in said first metal or alloy; and

(g) the resulting infiltrated part is cooled to
room temperature to form a substantially void-free
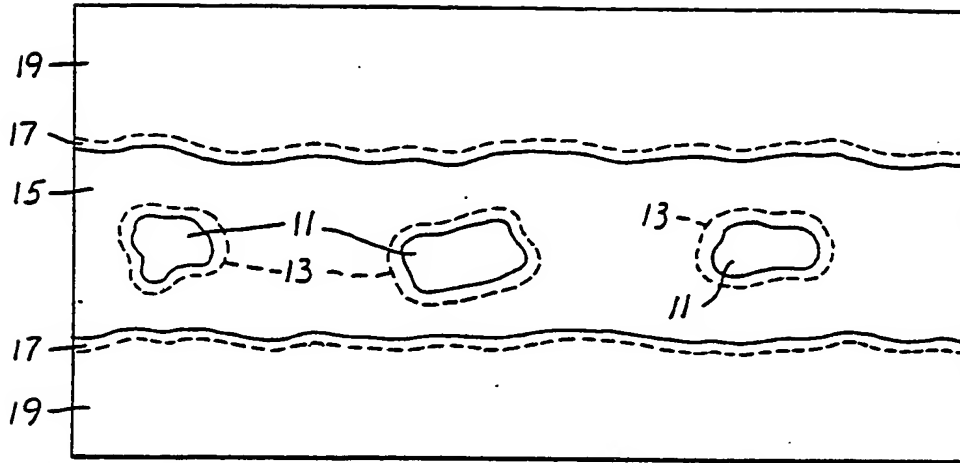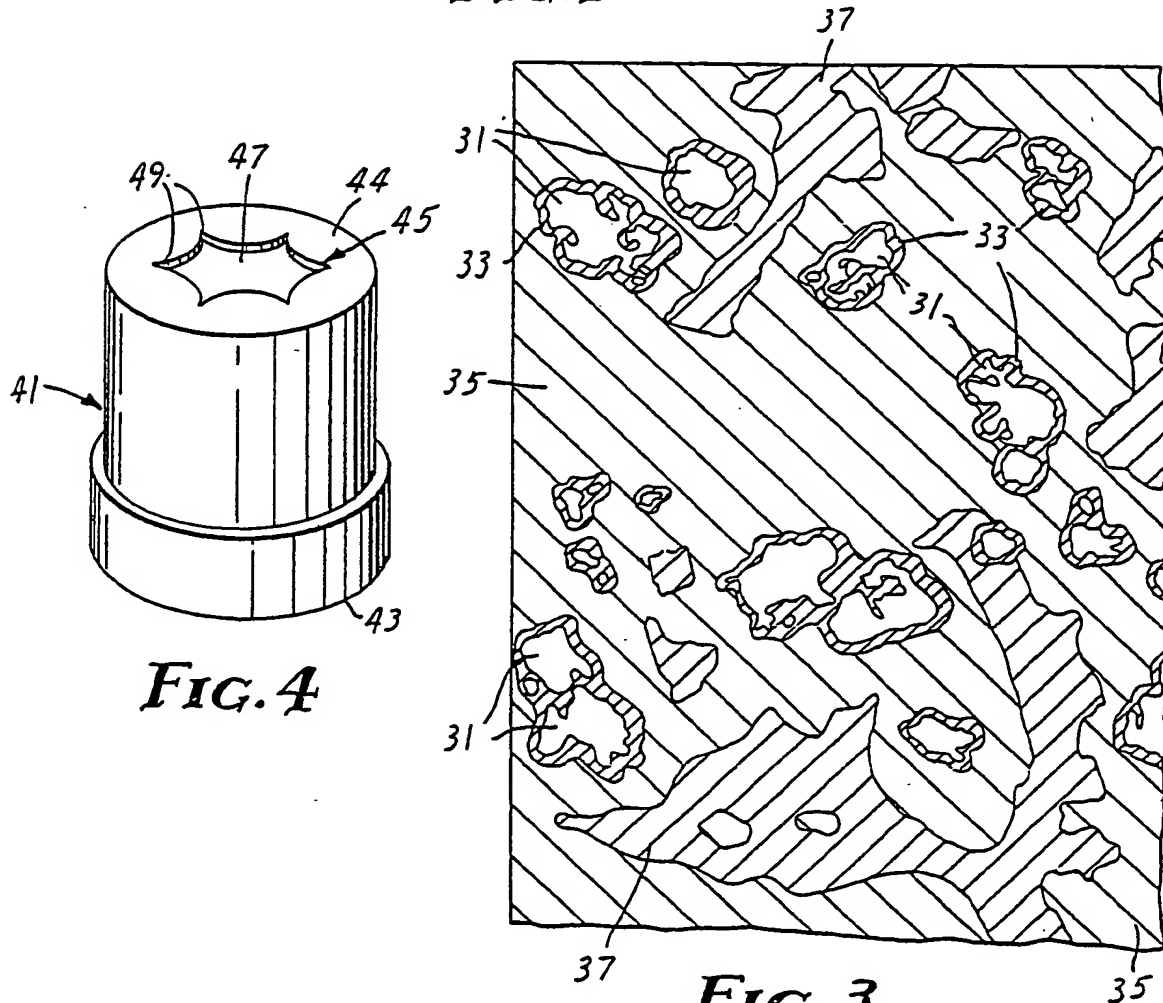
10   precision molded article.

FIG.1

FIG.4

FIG.3
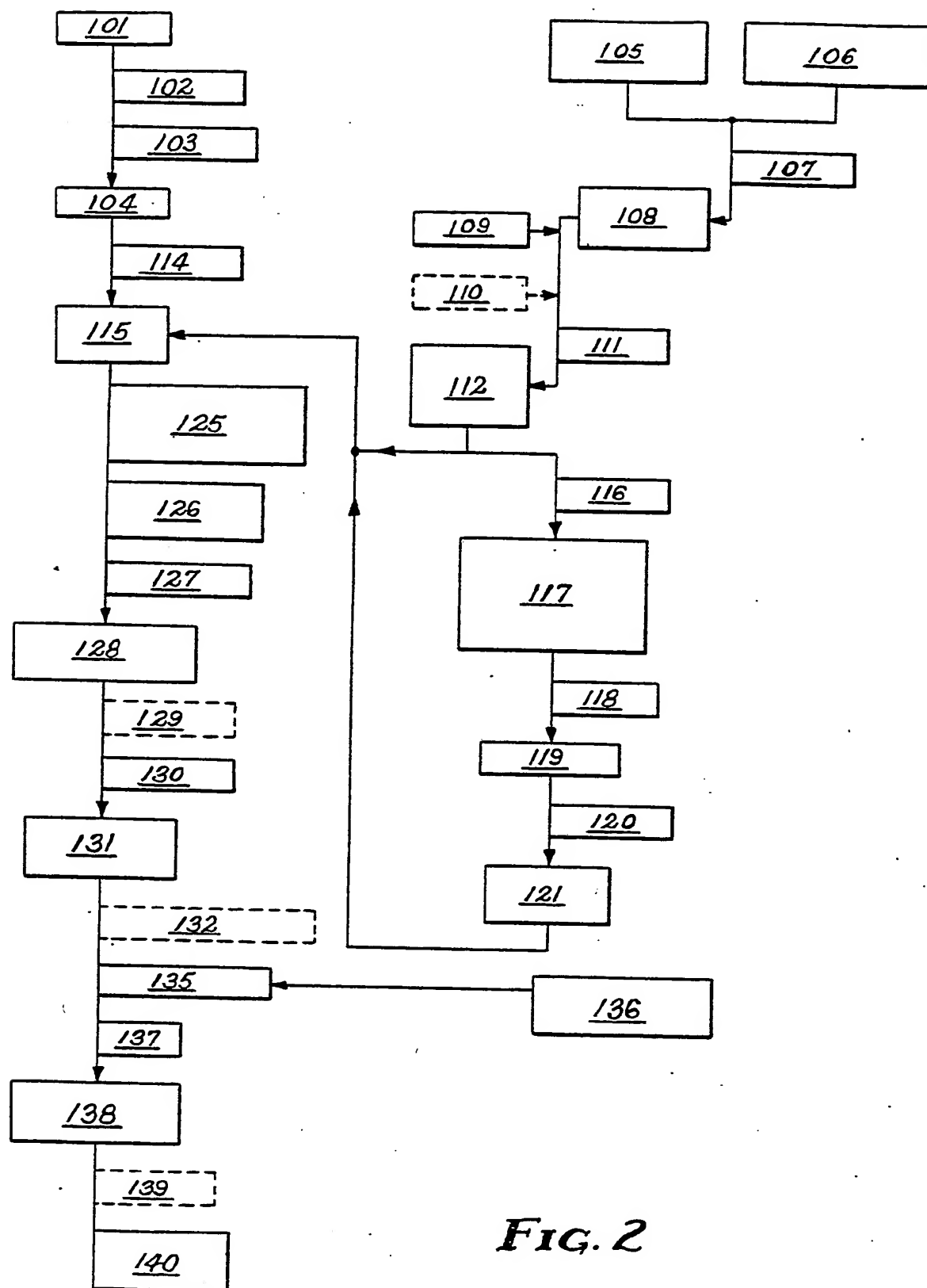
2 / 2

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No **PCT/US 81/00521**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

N./C. 428/568

IPC.⁰ B22F 3/26

II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
U.S.	428/568, 567, 545 75/203, 204, 208R, 200

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 5

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
X	US, A, 3,779,715 Published 18 December 1973 Wendler et al	1-10
A	US, A, 3,806,325 Published 23 April 1974 Niimi et al	1-10
A	US, A, 3,812,565 Published 28 May 1974 Seino et al	1-10

* Special categories of cited documents: 15

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2

3 August 1981

Date of Mailing of this International Search Report 2

06 AUG 1981

International Searching Authority 1

ISA/US

Signature of Authorized Officer 20

Form PCT/ISA/210 (second sheet) (October 1977)